

Phonons in mixed superionic fluorites $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$

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Abstract. In recent years, the fluorite-structured solid solutions with the general formula, $(\text{MF}_2)_{1-x}(\text{RF}_3)_x$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ and R is a rare-earth element or Y), have been the subject of numerous experimental studies focussed on their superionic properties. The overall cubic crystal symmetry (space group $Fm\bar{3}m$) is conserved up to $x \leq x_{\text{max}}$, where $x_{\text{max}} \approx 0.4\text{--}0.5$ depending on M and R . The zone centre phonons and phonon dispersion along three symmetry directions of the mixed superionic compound $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ have been investigated by applying de Launey angular force model for $x \leq x_{\text{max}}$. The calculated results are compared and explained with available experimental results.

Keywords. Superionic properties; $(\text{MF}_2)_{1-x}(\text{RF}_3)_x$; fast ion conductors.

1. Introduction

Fast ion conductors have been the subject of extensive research because of their interesting physical properties as well as their potential technological use (Hagenmuller and Van Gool 1978). High ionic mobility in a crystalline solid is a paradoxical requirement and it can only be achieved in the presence of disorder. Materials with fluorite structure can be disordered either by thermal activation (intrinsic conductors) or by doping with trivalent ions (extrinsic conductors) such as the lanthanide (Schoonman 1981). These systems are therefore, excellent candidates for studies of the mechanism of ionic transport in crystalline materials. In recent years, the fluorite-structured solid solutions with the general formula, $(\text{MF}_2)_{1-x}(\text{RF}_3)_x$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$, and R is a rare-earth element or Y), have been the subject of numerous experimental studies focussed on their superionic properties. The overall cubic crystal symmetry (space group $Fm\bar{3}m$) is conserved up to $x \leq x_{\text{max}}$, where $x_{\text{max}} = 0.4\text{--}0.5$ depending on M, R (Sobolev 1991). As in the pure fluorite structure crystals, the conductivity is due to hopping of mobile F^- anions (Kadlec *et al* 1999a).

A knowledge of the host lattice vibrations, being of fundamental interest in themselves, is of great importance and in some cases necessary in order to unravel and distinguish the pure electronic transitions from those which are vibronic in character. A complete understanding of the vibrational problem involves a knowledge of all the optical and acoustical branches. Therefore, in the present investigation mode behaviour of zone centre optical phonons in $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ for $0.01 \leq x \leq 0.47$ and phonon dispersion curves in all three symmetry directions of the mixed system $(\text{BaF}_2)_{0.84}(\text{LaF}_3)_{0.16}$ have been studied by applying a modified rigid ion model (MRIM) (Sinha *et al* 1995).

2. Crystal structure

The lanthanum doped BaF_2 crystals $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ exists in fluorite structure in the composition range $0 < x < 0.5$ (Kjems *et al* 1983). The one end member (BaF_2) of the mixed system is having fluorite structure (Manasreh and Pederson 1985), whereas the fluoride of La has the structure of the naturally occurring mineral tysonite (Bauman and Porto 1967). The lattice vibrations study and group theoretical analysis of LaF_3 reveal the fact that most of infrared and Raman modes of LaF_3 are inactive (Caspers *et al* 1964). So in the present study the lattice dynamics of mixed system $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ is investigated by assuming the other end member (LaF_3) of the mixed system as fluorite structure. The fluorite type lattice (BaF_2) consists of three *fcc* sublattices, one of barium ions (Ba^{2+}) and two of nonequivalent fluorine ions (F_1^- and F_2^-). The F_1^- and F_2^- sublattices are displaced along the body diagonal of the Ba^{2+} sublattice by $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $3a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, where a is the lattice constant. Each Ba^{2+} ion is at the centre of a cube with four F_1^- and four F_2^- ions at the corners and each F^- ion is at the centre of a tetrahedron with Ba^{2+} ions at the corners: the space group is O_h^5 and the primitive unit cell contains only one formula unit. For a one-phonon process, the displacement of the three ions in the unit cell transforms as $\Gamma = 2T_{1u} + T_{2g}$ at the Brillouin zone centre. The triply degenerate T_{2g} modes are Raman active modes due to the motion of F^- ions against each other, and one of the T_{1u} modes corresponds to three acoustic branches. The remaining triply degenerate T_{1u} modes split into a longitudinal optical modes (LO) and a doubly degenerate transverse optical mode (TO).

3. Theory

Many theoretical models have been proposed to explain and predict the mode behaviour of mixed systems (Sinha

1999). In the present investigation the phonons in mixed superionic fluorites has been studied by using a modified rigid ion model (MRIM), which consists of long range electrostatic and short range interactions up to third neighbours. The electrostatic contribution is derived on the lines of Kellermann (1940). The electrostatic contribution incorporates an effective charge to include the effect of the polarization which is determined using the Lyddane–Sachs–Teller (LST) relation (Hayes 1974). The short-range contribution to the dynamical matrix is derived by using de Launey (1956) type angular forces. The short-range interactions have three central and two noncentral force constants. Since the noncentral forces are small, they are being accounted for up to two neighbours only. The long-wavelength limit method has been used to establish the analytical relation between the force constants and elastic constants. The expressions for the phonon frequencies at the zone centre and the analytical relation between elastic and force constants thus obtained are given by the following equations

$$\frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1) + 4 \cdot 19(Z^2 e^2 / V_a \mathbf{e}_\infty) = [mM / (2m + M)] \mathbf{w}_{LO}^2, \quad (1)$$

$$\frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1) + 2 \cdot 095(Z^2 e^2 / V_a \mathbf{e}_\infty) = [mM / (2m + M)] \mathbf{w}_{TO}^2, \quad (2)$$

$$\frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1) + 4(\mathbf{a}_2 + \mathbf{a}'_2) = m \mathbf{w}_R^2, \quad (3)$$

$$2aC_{11} = \frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1) + 4\mathbf{a}_2 + 12\mathbf{a}_3 + 3 \cdot 0512(Z^2 e^2 / V_a \mathbf{e}_\infty), \quad (4)$$

Table 1. Input data taken from Hurrell and Minkiewicz (1970), Laiho *et al* (1983), Manasreh and Pederson (1985) and Kadlec *et al* (1999b).

Compound	Elastic constants (10^{10} Nm^{-2})			Zone centre frequencies (cm^{-1})		
	C_{11}	C_{12}	C_{44}	\mathbf{w}_{LO}	\mathbf{w}_{TO}	\mathbf{w}_R
BaF ₂	9.244	4.212	2.536	326	184	258
LaF ₃	18.00	8.80	3.400	465	355	400

Table 2. Calculated force constants and effective charge.

Compound	Force constants (Nm^{-1})					Effective charge
	\mathbf{a}_1	\mathbf{a}'_1	\mathbf{a}_2	\mathbf{a}'_2	\mathbf{a}_3	Z_{eff}
BaF ₂	50.19	-5.87	4.77	0.60	1.10	1.623
LaF ₃	113.4	-4.89	4.25	3.16	-8.34	0.245

$$2aC_{12} = \frac{4}{3}(\mathbf{a}_1 - 4\mathbf{a}'_1) - 4\mathbf{a}'_2 + 6\mathbf{a}_3 - 5 \cdot 4046(Z^2 e^2 / V_a \mathbf{e}_\infty), \quad (5)$$

$$2aC_{44} = \frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1) + 4\mathbf{a}'_2 + 6\mathbf{a}_3 - 1 \cdot 5256(Z^2 e^2 / V_a \mathbf{e}_\infty) \frac{\{\frac{4}{3}(\mathbf{a}_1 - \mathbf{a}'_1) - 5 \cdot 02884(Z^2 e^2 / V_a \mathbf{e}_\infty)\}^2}{\frac{4}{3}(\mathbf{a}_1 + 2\mathbf{a}'_1)}. \quad (6)$$

Here \mathbf{a}_1 and \mathbf{a}'_1 represent the central and angular force constants between Ba and F_1^- or F_2^- , whereas \mathbf{a}_2 and \mathbf{a}'_2 represent the central and angular force constants between F_1^- and F_2^- ions, respectively. The central force constant between Ba^{2+} – Ba^{2+} ions is assumed to be the same as that between F_1^- – F_1^- or F_2^- – F_2^- ions and is represented by \mathbf{a}_3 . Here Ze is the charge on cation and $-Ze/2$ on fluorine ion, V_a the volume of the unit cell and \mathbf{e}_∞ the

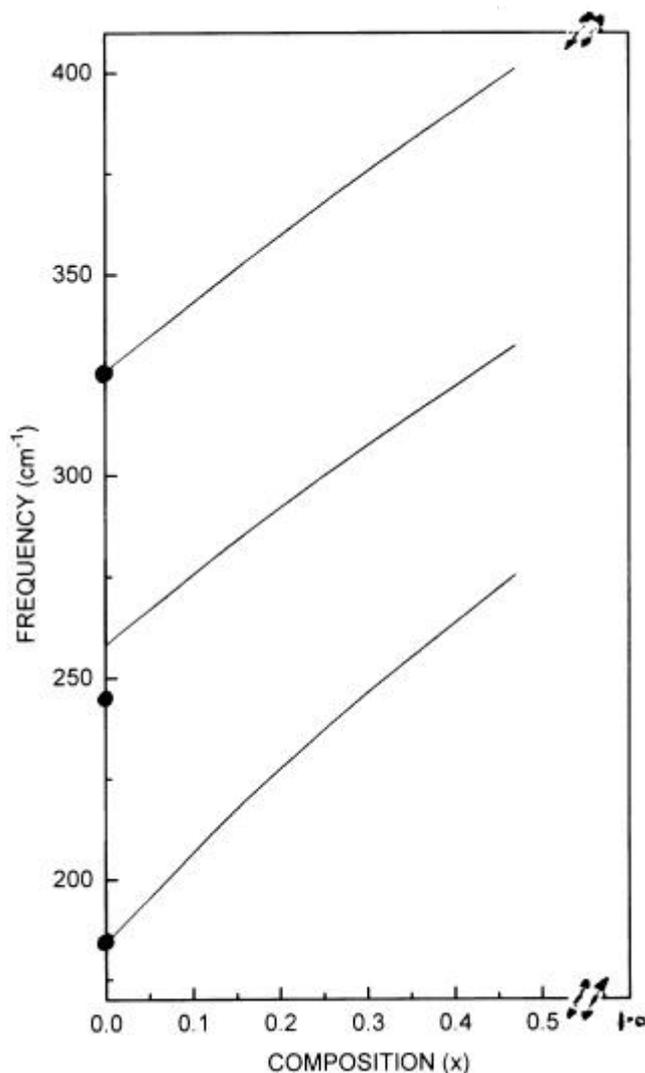


Figure 1. Compositional variation of optical phonons at zone-centre in mixed $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ system.

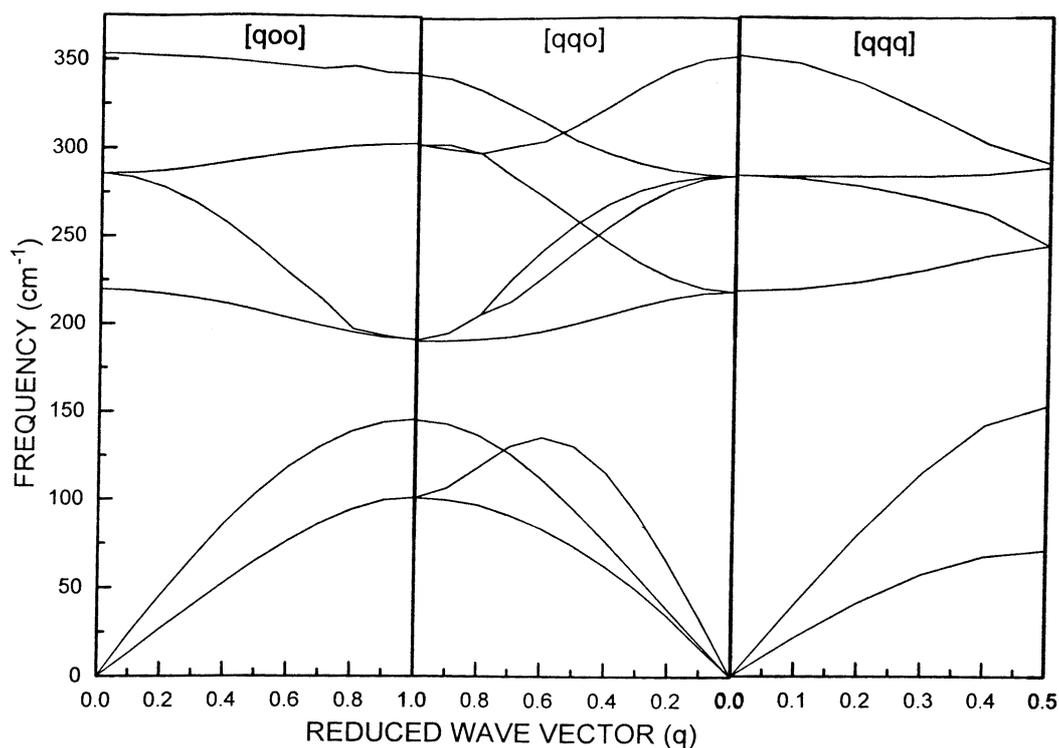


Figure 2. Phonon dispersion curves of $(\text{BaF}_2)_{0.84}(\text{LaF}_3)_{0.16}$.

high frequency dielectric constant. The effective charge, Z_{eff} ($Z_{\text{eff}}^2 = Z^2/\epsilon_{\infty}$), is evaluated with the help of the LST relation given by

$$Z_{\text{eff}}^2 = \frac{mV_a(w_{\text{LO}}^2 - w_{\text{TO}}^2)}{2pe^2}.$$

Here m is the reduced mass ($1/m = 1/m + 2/M$), m being mass of the fluorine ion and M the mass of barium. w_{LO} and w_{TO} represent the infrared optical frequencies whereas w_{R} is the Raman active mode at zone centre.

The force constants (\mathbf{a}), masses (m), lattice constants and effective charge (Z_{eff}) of mixed fluorites are calculated by assuming the linear variation from one end member to the other with composition, x (Gupta *et al* 1987) as given below

$$\mathbf{a}[(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x] = \mathbf{a}(\text{BaF}_2) \times (1-x) + \mathbf{a}(\text{LaF}_3) \times x. \quad (7)$$

4. Results and discussion

The input data of the elastic constants and zone centre frequencies taken for the determination of the effective charge and force constants are listed in table 1. Substituting these input data in the above equations except (2), the short-range force constants and effective charge are calculated in table 2. The force constants, effective charge, masses and lattice parameter of the mixed system

$(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ is calculated by using (7). The variation of infrared-active and Raman active zone centre phonon frequencies with composition (x) is shown in figure 1 along with experimental results (Kadlec *et al* 1999b). From figure 1 it is very clear that zone-centre phonons vary linearly with composition for mixed system up to which the fluorite structure is conserved. The present calculation therefore, predicts one mode behaviour in mixed system $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ for $0 < x < 0.5$. The phonon frequencies along the three main symmetry directions are calculated for the mixed system $(\text{BaF}_2)_{0.84}(\text{LaF}_3)_{0.16}$ and are shown in figure 2. Comparison of results could not be possible because of lack of experimental data.

References

- Bauman R P and Porto S P S 1967 *Phys. Rev.* **B161** 842
- Caspers H H, Buchanan R A and Marlin H R 1964 *J. Chem. Phys.* **41** 94
- De Launey J 1956 *Solid State Phys.* **2** 219
- Gupta H C, Sinha M M and Tripathi B B 1987 *Solid State Commun.* **62** 777
- Hagenmuller P and Van Gool W (eds) 1978 *Solid electrolytes* (New York: Academic Press)
- Hayes W 1974 *Crystals with the fluorite structure* (Oxford: Clarendon Press)
- Hurrell J P and Minkiewicz V J 1970 *Solid State Commun.* **8** 463
- Kadlec F, Moussa F, Simon P and Sobolev B P 1999a *Solid State Ionics* **119** 131

- Kadlec F, Simon P and Raimboux N 1999b *J. Phys. Chem. Solids* **60** 861
- Kellermann E W 1940 *Philos. Trans. Roy. Soc.* **A238** 513
- Kjems J K, Andersen N H, Schoonman J and Clausen K 1983 *Physica* **B120** 357
- Laiho R, Lakkisto M and Levola T 1983 *Philos. Mag.* **A47** 235
- Manasreh M O and Pederson D O 1985 *Phys. Rev.* **B31** 3960
- Schoonman J 1981 *Solid State Ionics* **5** 71
- Sinha M M 1999 *Nucl. Instrum. Meth. Phys. Res.* **B153** 183
- Sinha M M, Ashdhir P, Gupta H C and Tripathi B B 1995 *Phys. Status Solidi (b)* **191** 101
- Sobolev B P 1991 *Bull. Soc. Cat. Cien.* XII 275